Kinetics of silicide formation by thin films of V on Si and SiO_2 substrates*

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The reaction rate of vacuum-evaporated films of V of the order of 1000 Å thick is investigated by MeV He backscattering spectrometry. On substrates of single-crystal Si and for anneal times up to several hours in the temperature range 570–650 °C, VSi_2 is formed at a linear rate in time. The activation energy of the process is 1.7 ± 0.2 eV. The presence of oxygen in amounts of 10% can significantly decelerate the reaction. On substrates of SiO_2 in the temperature range 730–820 °C and anneal times of several hours or less, V_3Si is formed at a square-root rate in time. The activation energy of this process is 2.0 ± 0.2 eV.

I. INTRODUCTION

Thin deposited films can exhibit enhanced reactivity. Recognition of this fact and its practical implications have generated a desire for detailed information in thin-film reactions. The main points of interest are the origin of the forces which drive a reaction, the kinetics, and the resulting products.

The interaction of metal films with Si has attracted considerable attention already. It is now known that films of silicide-forming transition metals react with a Si substrate and form the thermodynamically stable Si-rich compound at temperatures which are typically one-half of the melting point of the compound temperature. The kinetics of these reactions has been studied so far for Pd and Cr,[1] Hf,[2] and V.[3] The formation of Pd_2Si, HfSi, and VSi_2 is reported to follow a $(\text{time})^{1/2}$ dependence, while $CrSi_2$ forms linearly with time.

The interaction of metal films with SiO_2 belongs to the class of ternary systems and is more complicated than the binary reactions. Experimental data have been published for V,[3–6] Ti,[5,6] and Nb.[5,6] They show that SiO_2 dissociates under the metal film, resulting in the formation of a new intermediate layer of a metal-rich silicide, while the oxygen originally bound to the Si is transferred to the remaining metal. No reaction rates have been reported for these ternary processes.

We present here an experimental study of the reaction rates of V films on Si and on SiO_2 substrates. In contrast to Tu *et al.*,[3] we observe a linear reaction rate for the silicide formation on Si, but oxygen is shown to decelerate the reaction noticeably. The resulting silicide layer has the composition VSi_2. On SiO_2 substrates, the growth rate of the silicide layer is proportional to $(\text{time})^{1/2}$. The composition of that layer is V_3Si, which again agrees with earlier observations.

II. EXPERIMENTAL PROCEDURES

Commercially prepared and polished wafers of single crystals were used as Si substrates. The wafers were lightly etched in CP-4 and rinsed in HF and deionized water immediately prior to being placed in the dry vacuum system. The electron-gun evaporation of V was performed at a vacuum of 2×10^{-7} Torr. The V film was deposited simultaneously on the unheated Si wafer and on a test wafer of vitreous carbon, which served as a monitor to detect spurious elements such as oxygen. After evaporation, the samples and the carbon monitor were analyzed by MeV He backscattering spectrometry.[7] For the experiments with SiO_2 substrates, the Si wafers were thermally oxidized at 1100 °C in wet oxygen. Typical thicknesses used ranged from 2000 to 3000 Å of SiO_2.

Anneals were performed in a 1-in diffusion furnace with an evacuated quartz tube. The typical vacuum during anneals was better than 5×10^{-6} Torr. To prevent contamination by oxygen, it was necessary to add a Ti sublimation pump at one end of the quartz tube. This pump was activated for 1 min prior to inserting a sample into the furnace. All samples used in the study were inspected with optical microscopes or a SEM for their lateral uniformity.

III. V FILMS ON Si SUBSTRATES

A. Linear growth of VSi_2

Typical backscattering spectra obtained on a sample consisting of a *n*-type Si substrate oriented in the ⟨100⟩ direction with a 2000-Å film are shown in Fig. 1 before and after anneal. The fact that the V film is free of any significant concentration of contaminants can be seen directly in the spectrum of the unannealed sample by comparing the step height of the V signal at its low-energy edge (~1.15 MeV) to the step height of the Si signal at its high-energy edge (~0.85 MeV). The height of the signal from the unreacted V film remains unchanged

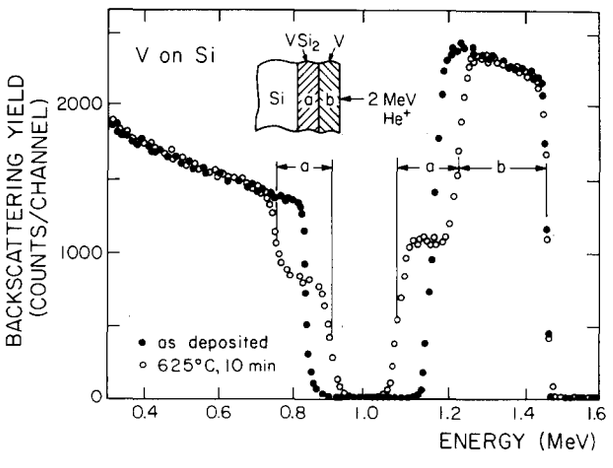


FIG. 1. Backscattering spectra of a 2000-Å film of V evaporated on a {100} plane of a Si single crystal before (full dots) and after (open circles) vacuum anneal measured with 2-MeV $^4He^+$.

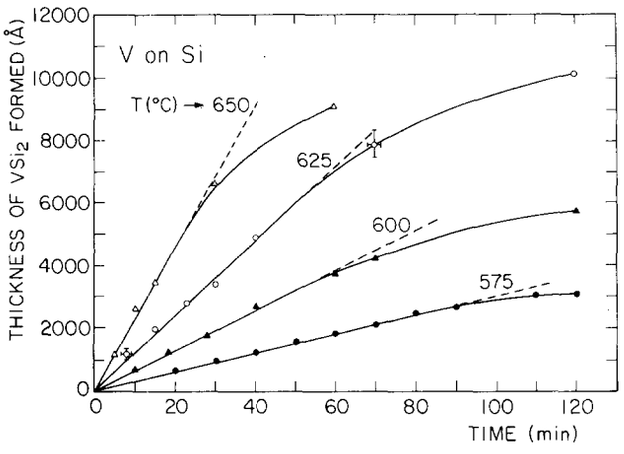


FIG. 2. Isothermal anneal curves for the formation of VSi_2 (layer a of Fig. 1).

during annealing. This excludes the possibility of significant contamination of the film during the anneal. The analysis of the carbon monitors established that no more than 3% of oxygen was present in the original metal film.

The formation of an intermediate layer is revealed in Fig. 1 by the appearance of an intermediate step on the low-energy side of the V signal and on the high-energy side of the Si signal. The widths of these steps are a measure of the thickness of this new layer, and the amplitude ratio of the two steps is a measure of the atom ratio in the layer. This ratio is found to be V : Si = 1 : 2. X-ray measurements have established the phase of this intermediate layer as pure VSi_2.[6] By measuring the widths of either steps after isothermal anneals of increasing duration, we obtained the rate of compound formation at that temperature. Figure 2 shows the results of such measurements performed at various temperatures. The thickness of the VSi_2 layer plotted as the ordinate is derived from the width of the corresponding step in the backscattering spectrum of Fig. 1 according to the procedure given by Chu *et al.*[7,8]

Figure 2 shows a linear reaction rate with time, over the temperature range 570—650 °C and for anneal times between 5 min and 2 h. These results were reproducible as long as the contamination of the metal film by oxygen was prevented, and as long as the substrate surface was clean prior to film deposition. The same linear rate was obtained for Si substrates oriented in the ⟨111⟩, ⟨100⟩, and ⟨110⟩ direction, for either conductivity type or for wafers which were sputter cleaned by keV Ar^+ immediately prior to the e-gun evaporation. Typical experimental errors are shown at a few points. The uncertainty in the temperature values is about ±4 °C and is determined largely by the nonuniform temperature profile of the furnace.

From Fig. 2, one can derive the Arrhenius plot of Fig. 3, which shows that in that temperature range the formation of VSi_2 is thermally activated with an activation energy of $\Delta E = 1.7 \pm 0.2$ eV. At 600 °C, the reaction rate is thus described by the relationship $v = v_0 \exp \times(-\Delta E/kT)$, with $v_0 = 75$ cm/s.

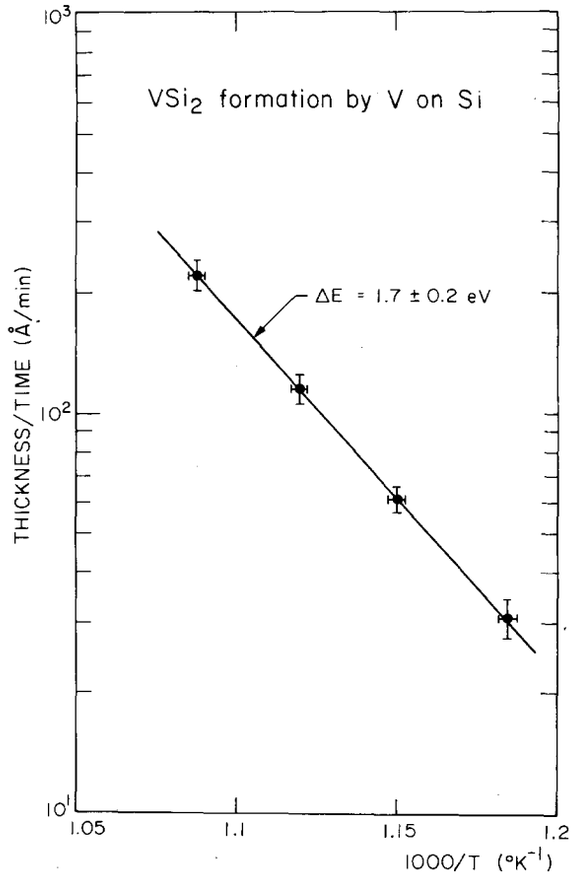


FIG. 3. Arrhenius plot for the linear portion of the isothermal growth curves at VSi_2 shown in Fig. 2.

B. Nonlinear growth of VSi_2

Tu *et al.*[3] report a nonlinear (time)$^{1/2}$ dependence of growth for VSi_2, give an activation energy of 2.9 eV for the process, and a diffusion constant of 2.9×10^{-15} cm^2/s at 600 °C. We have observed nonlinear growth also. This is shown in Fig. 4, where the thickness of the VSi_2 layer and the anneal time are plotted logarithmically for various temperatures. Examination of this figure points out the following two facts: (i) The existence of a linear range is evident, even after allowance of the experimen-

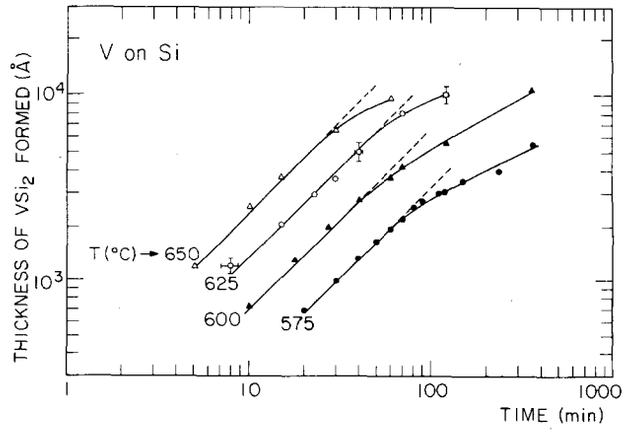


FIG. 4. Log-log plot of the isothermal growth rate of VSi_2. The rate becomes nonlinear for long anneal times (see text).

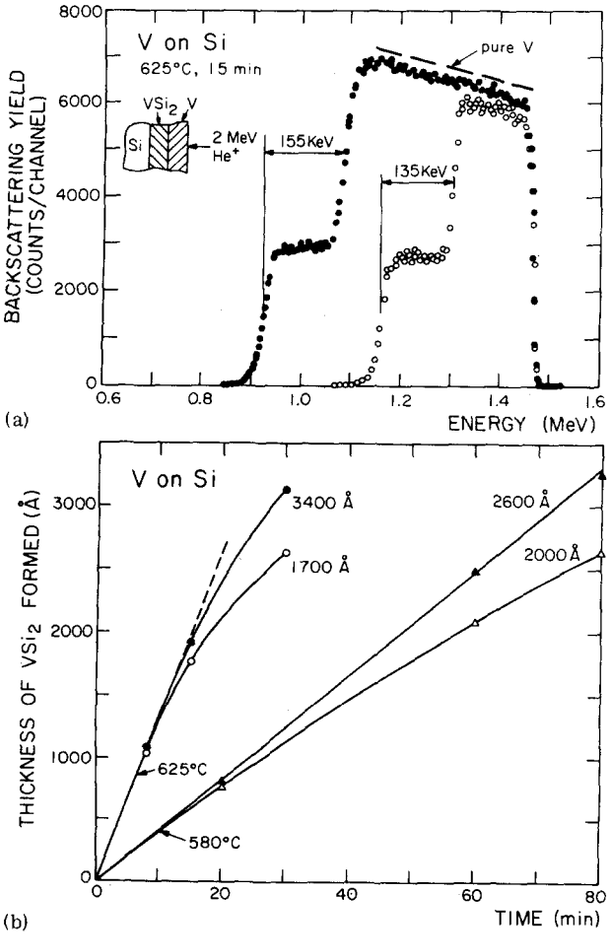


FIG. 5. (a) The V signal of two backscattering spectra of a 1700- and 3400-Å V film on Si. The films are contaminated with oxygen, as can be seen from the height of the spectra, which do not reach that of pure V (dashed line). A simultaneous anneal of the two films for 15 min at 625 °C generates VSi_2 layers of different thicknesses. (b) Oxygen-contaminated V films on Si exhibit nonlinear rates of VSi_2 growth. The effect depends on the initial thickness of the film and the oxygen content (see text).

tal errors shown at a few points, and (ii) the nonlinearity is most pronounced for long anneals and thin films.

Contaminations introduced in the film during anneal could produce such an effect, and oxygen is a prime suspect for vanadium. Since backscattering spectrometry is not very sensitive to oxygen in the presence of a substrate such as Si, an increase in oxygen sufficient to interfere with the reaction could well occur without being detected by backscattering. We have therefore undertaken a series of measurements with V films in which oxygen was deliberately introduced, or known to be present after the deposition of the film. Two films of 1700- and 3400-Å thickness and with approximately 10% oxygen distributed uniformly throughout each film were deposited on Si. Both samples were then annealed simultaneously for 15 min, and the samples were analyzed. Figure 5(a) shows the V signals of the two backscattering spectra. The unreacted (top) part of the metal films generate signal heights which are lower than that of a pure V film (dashed line). This proves that the metal is indeed contaminated. The spectra show that the thicker metal film has formed a 15% thicker layer of silicide than the thinner film. That last result is expected if oxygen contamination decelerates the growth rate. As the reaction initially proceeds at a common rate, the oxygen concentration in the unreacted metal film increases more rapidly in the thinner of the contaminated films, thus slowing down the growth rate sooner in the thinner film [Fig. 5(b)]. A larger final contamination of the residual metal layer in the thinner film can also be seen in the spectra of Fig. 5(a) where the signal heights of the unreacted V is lower for the thinner sample, which indicates a larger concentration of impurities.

We have also compared the growth of silicide layers under identical anneal treatments obtained by V films of about 2000-Å thickness, but with and without measurable oxygen contamination after the deposition of the film [Fig. 5(b)]. It is found that initially the two films have identical reaction rates with the Si substrate, but with time the contaminated films react progressively slower than the pure films.

The silicide thicknesses we observed in oxygen-free films are much larger than those reported by Tu *et al.* under comparable conditions.[3] This suggests that those samples contained oxygen.

IV. V FILMS ON SiO_2 SUBSTRATES

Films between 2000 and 4000 Å of V have been annealed in the temperature range 730—820 °C. This is about 200 °C above the temperatures used for the V films on Si substrates. Below about 700 °C, the reaction with SiO_2 becomes inconveniently slow. It must be noted also that V_2O_5 melts at about 680 °C and undergoes transformation in vacuum.[9] Vanadium films oxidized at low temperatures (about 400 °C) undergo destructive changes when annealed above this melting point. For that reason too, temperatures in the vicinity of 680 °C have been avoided.

Figure 6 shows a backscattering spectrum of a 2000-Å film after anneal at 820 °C for 30 min. The dashed line is the spectrum before anneal. The main feature is the growth of a new intermediate layer during anneal at the SiO_2-V interface (labeled b). The composition of this layer, as deduced from the heights of the corresponding V and Si signals, is V_3Si, in agreement with x-ray data.[5,6] The total area of the oxygen signal (which is

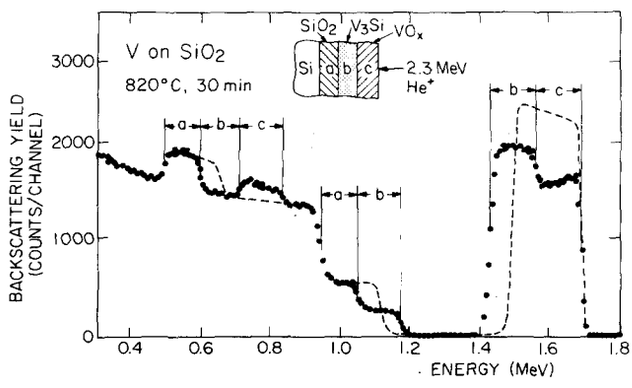


FIG. 6. Backscattering spectra of a 2000-Å V film before (dashed line) after anneal at 820 °C for 30 min.

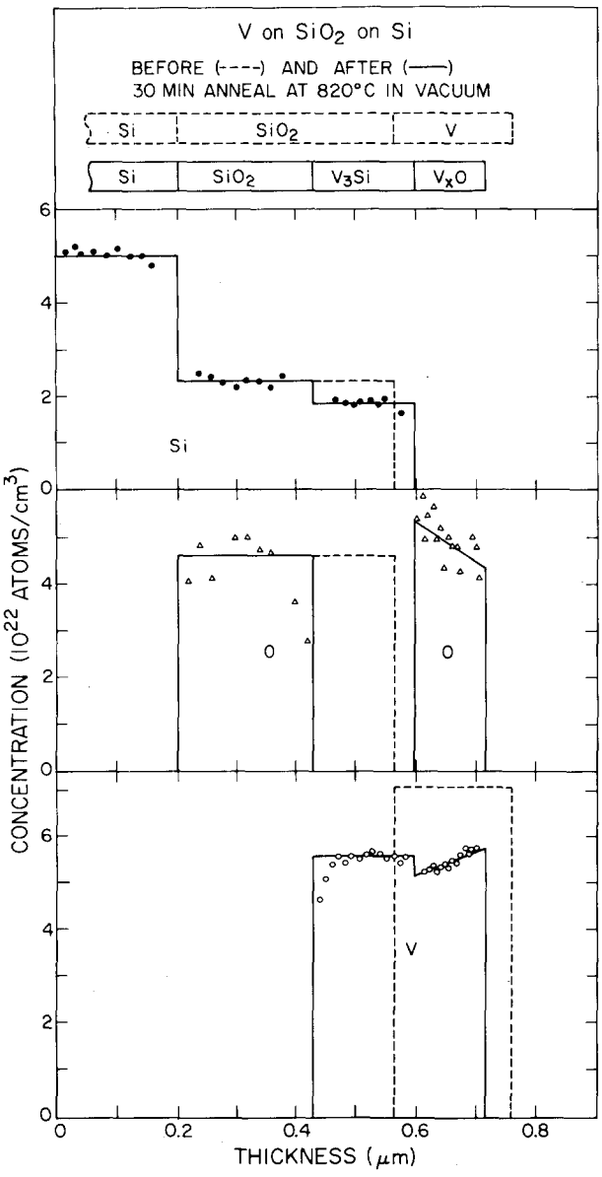
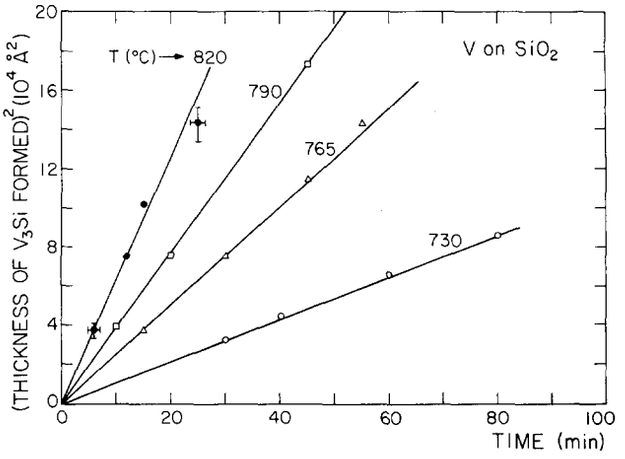


FIG. 7. Concentration profile of O, Si, and V obtained from the spectra of Fig. 6. Solid lines give the profiles after anneal, dashed lines give those before heat treatment.

superimposed on that of the Si substrate) is the same before and after anneal. This proves that the total amount of oxygen present remains constant during anneal. But after the heat treatment, that fraction of the oxygen which was originally bound to the Si in the V_3Si is found in the remaining V layer (labeled c). The oxygen concentration in that layer is nonuniform and is lowest at the surface of the film. Figure 7 gives a straight-line plot of concentration profiles as they are calculated from the two spectra of Fig. 6.[7,8]

We have measured the rate of growth of the intermediate V_3Si layer (b) as a function of anneal time at various temperatures. The result is given in Fig. 8 and shows a $(\text{time})^{1/2}$ dependence, characteristic of diffusion-limited growth. We estimate the diffusion constant at 790°C to be $D=6.2\times10^{-14}$ cm^2/s according to the equation $D=x^2/t$ with $x=860$ Å for $t=20$ min. From Fig. 9, one deduces an activation energy of $\Delta E=2.0\pm0.2$ eV



FIG;8. Isothermal anneal curves for the formation of V_3Si (layer b of Fig. 6).

for the process. The diffusion constant can thus be expressed as $D=D_0\exp(-\Delta E/kT)$ with $D_0=2.0\times10^{-4}$ cm^2/s.

The growth of the V_3Si layer always comes to a fairly sudden stop, even when the SiO_2 is not depleted. We attribute this termination of the reaction to a saturation of the remaining V by oxygen. Termination is observed whenever the O-to-V ratio at the V_3Si interface reaches

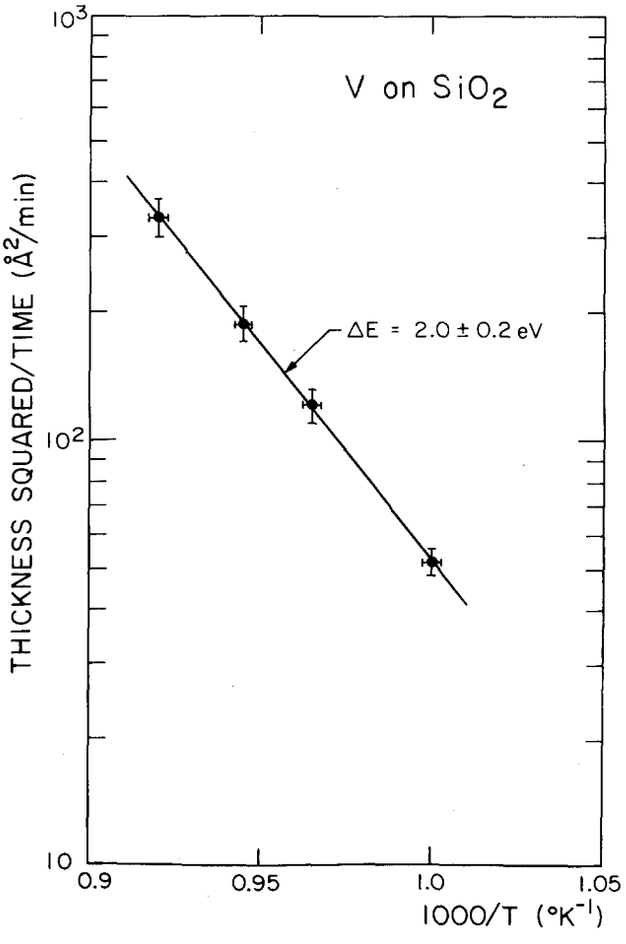


FIG. 9. Arrhenius plot for the isothermal growth curves of V_3Si shown in Fig. 8.

a value of about 1:1. For example, the sample shown in Figs. 6 and 7 do not react further when annealed for 30 min more or when heated to 850°C, but the growth would have proceeded beyond its present point for a thicker initial V layer and would have stopped short of it for a thinner metal layer. Indications of this growth limit are also visible in Fig. 8. The point of saturation is reached when approximately three-fifths of the metal film has been transformed to V_3Si.

If the SiO_2 layer is fully consumed before the oxygen saturation of the V is reached, the reaction also stops. To induce further changes in the layers, temperatures in excess of <1000°C are required, at which point deep localized pits will develop in the film, indicating sudden intensive reaction with the Si substrate.

V. DISCUSSION AND SUMMARY

The results presented here have been obtained by backscattering spectrometry. This method provides atomic concentration ratios and is sufficiently sensitive so that films above ≈ 200 Å can be analyzed. This information is sufficient for studies of kinetics. The identification of the phases by x-ray diffraction has been carried out previously.[6]

For V on Si, the growth of VSi_2 begins linearly with time in contrast with earlier results which indicated a $(\text{time})^{1/2}$ dependence. However, we also observed nonlinear growth rates. Samples in which the nonlinear growth was observed contained contaminants. In some cases, oxygen was identified as impurity. It was known before that oxygen contaminations at the metal-silicon interface can interfere strongly with the formation of silicides by metal films.[1] Our results now establish that the presence of oxygen in the metal film can cause similar effects.

The activation energy of 1.7 eV is lower by 0.5—1.0 eV than energies commonly observed for silicide reactions at about 600°C. One would therefore expect that this reaction would occur at lower temperatures as well. An effort was made to follow the process at lower temperatures and longer anneal times. We found that in one case at 550°C and 133 min the thickness of the reacted layer (2600 Å) conformed with the dependence shown in Fig. 3. In other cases, where anneal times become long, oxygen contaminated the film and growth was decelerated.

Linear rates of silicide formation have been reported for $CrSi_2$ [2] and WSi_2 [10] commonly attributed to reaction-limited growth. Eventually, transport-limited growth will dominate the process and lead to a $(\text{time})^{1/2}$ dependence. In contrast to conventional metallurgical methods of analysis, backscattering spectrometry has a sensitivity and depth resolution which gives ready access to the thickness ranges where reaction-limited processes can dominate.

For SiO_2 substrates, the growth rate of the V_3Si goes with the square root of time. The backscattering spectra indicate that the V_3Si layer is highly uniform in thickness and composition. The oxygen originally bound to the Si in the newly formed V_3Si layer is transferred to the remaining V layer overlaying the silicide. The reaction is halted if the atomic oxygen concentration in the V reaches a ratio at about O:V = 1:1. The reaction is also terminated upon consumption of the SiO_2 layer. The activation energy for V_3Si formation on SiO_2 appears low, but the number of available activation energies for silicide formations by thin-film reactions is too small for a systematic comparison.[11]

It would be desirable to have microscopic models to explain the different nature of the rates and of the final products of the reactions described here. In addition to information on the driving forces of these reactions, about which very little is known as facts, it would be useful to have some understanding of the relative mobility of the various species in the various layers. Marker experiments can provide such information. Further experiments are underway in this direction.

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[8] We have used $[S]^{Si}_{VSi_2} = 79$ eV/Å, $[S]^{V}_{VSi_2} = 77$ eV/Å, $[S]^{Si}_{V_3Si} = 84$ eV/Å $= [S]^{V_3}_{V_3Si}$, $[S]^{O}_{SiO_2} = 48$ eV/Å, $[S]^{Si}_{SiO_2} = 51$ eV/Å, $[S]^{O}_{O} = 26$ eV/Å, $[S]^{Si}_{Si} = 45$ eV/Å, and $[S]^{V}_{V} = 97$ eV/Å.
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